



Electroorganic reactions. Part 57.[†] DDQ mediated anodic oxidation of 2-methyl- and 2-benzyl-naphthalenes

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Abstract

Electron-rich 2-methyl and 2-benzyl-naphthalenes are efficiently converted into the corresponding carboxaldehyde or ketone by mediated electrolysis in the presence of about 25 mol % of DDQ. The reaction conditions are simple (constant current, undivided cell of 500 ml volume, graphite electrodes, aqueous acetic acid at 80 °C) and the construction of a reaction profile (products vs charge) shows the intermediate formation of side-chain acetoxy and hydroxy derivatives and the parallel formation of a byproduct involving side-chain substitution by DDQ.

1. Introduction

Alkylaromatics may be directly anodically oxidised in nucleophilic solvents to nuclear and side-chain substituted products and in non-nucleophilic media dimerisation and other combination reactions are favoured [1–3]. Nuclear substitution in methanol often leads to further, *ipso*, substitution eventually to give quinone ketals [4, 5]. The side-chain oxidation process may be operated on a relatively large scale as exemplified by a recently reported [6] ‘paired electrosynthesis’ with the conversion of 4-*t*-butyltoluene into 4-*t*-butylbenzaldehyde as the anodic component.

Derivatives of naphthalene-2-carboxaldehyde may be elaborated to give analogues of compounds with useful biological activity, including nonsteroidal anti-inflammatory compounds. The anodic conversion of 2-methyl naphthalenes into the 2-carboxaldehyde would therefore be of industrial interest. In this context we recently [7] explored the direct anodic oxidation in nucleophilic media of many 2-methyl and 2-benzyl-naphthalenes, substituted at the 6-position in the naphthalene nucleus and at the 4-phenyl position of the benzylic side chain, in order to identify factors favouring side-chain substitution. We found [7] that in almost all cases, irrespective of the electron demand at the benzylic position, nuclear substitution or dimerisation was favoured over side-chain substitution. However, batch oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acetic acid smoothly converted [7] electron-rich 2-methoxy-6-methylnaphthalene (**1a**) into the corresponding carbonyl derivatives. Oxidation with DDQ in aqueous acetic acid

at 80 °C gave high yields (>90%) of the corresponding aldehyde **2** for the substrates **1a**, **1k**, and **1l** and a moderate yield (50%) from **1b**. These reactions demanded a three-fold excess of DDQ; for **1a** oxidation with a 1:1 ratio of substrate:DDQ gave a 70% yield of the adduct **5a**.

In such reactions DDQ is itself reduced to the corresponding hydroquinone (DDQH₂) and this in turn may be reoxidized anodically to DDQ. Consequently the use of DDQ as an oxidant, in nonstoichiometric quantities, and its *in situ* anodic regeneration may be the basis of a useful process that could be scaled up. We report here on experiments seeking to optimise conditions for such conversions.

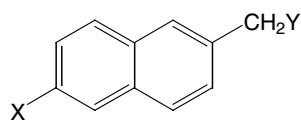
2. Experimental details

The synthesis of all starting materials and the full characterization of all products were described earlier [7].

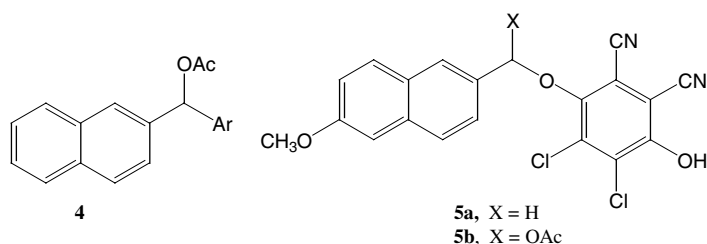
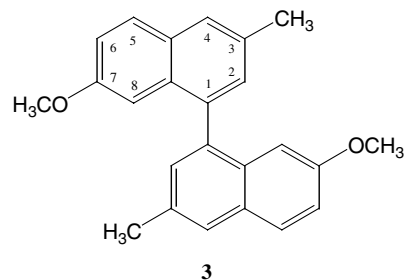
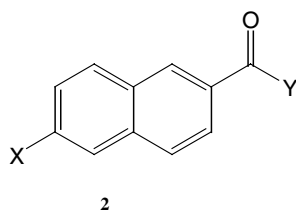
HPLC-UV analytical experiments were conducted using a KippAnalytica, 9209 Autosampler connected to a ConstaMetric III pump, feeding a PhaseSep, Spherisorb S5 ODS2 (25 cm × 4.6 mm) Reverse phase column. A Spectromonitor III, model 1204A set at 240 nm, was used as the u.v.-detector and the chromatograph recorded on a Shimadzu, Chromatopac C-R1B. Flash chromatography was performed using Sorbsil C 40/60H silica gel. Thin layer chromatography was performed using Merck DC-Alufolien Kieselgel 60 F₂₅₄ plates with a thickness of 0.2 mm.

Cyclic voltammetric experiments (CV) were performed using a VersaStat EG&G Princeton Applied Research potentiostat with model 270/250 ‘Research Electrochemistry Software’ (v 4.00).

[†] For part 56 see [7].



- 1a**, X = OCH₃, Y = H
1b, X = CH₃, Y = H
1c, X = H, Y = C₆H₅
1d, X = H, Y = 4-CH₃.C₆H₄
1e, X = H, Y = 4-CH₃O.C₆H₄
1f, X = H, Y = 4-Cl.C₆H₄
1g, X = CH₃O, Y = C₆H₅
1h, X = CH₃O, Y = 4-CH₃.C₆H₄
1i, X = CH₃O, Y = 4-CH₃O.C₆H₄
1j, X = CH₃O, Y = 4-Cl.C₆H₄
1k, X = CH₃O, Y = OH
1l, X = CH₃O, Y = OAc



The cells and electrodes for cyclic voltammetry, including reference electrodes were as described earlier [7].

The solvents used were normally freshly distilled and kept over freshly activated molecular sieves to ensure dryness. Tetraethylammonium tosylate was recrystallised from ethanol and dried in an oven (70 °C, 25 mm Hg) for at least 24 h prior to use.

Preparative scale electrochemical reductions were carried out using a DT 2101 Hi Tek potentiostat with an electronic charge integrator constructed in the Department's electronic workshop.

2.1. General procedure A (small scale)

An undivided cell of conventional design was used equipped with magnetic stirrer, two graphite rods (dia. 5 mm, with a working area of about 2 cm², as working and counter electrode) and an Ag/AgBr reference electrode positioned as close as possible to the working electrode. The electrolyte, a solution containing acetic acid, water and supporting electrolyte was heated to 80–90 °C and the substrate (typically between 2.5 and 5.0 mmol) added. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or the hydroquinone (DDQH₂) was added in portions. With DDQ the reaction mixture rapidly turns dark green (charge transfer complexation) followed by development in about 30 mins of a pink–red colour (2,3-dichloro-5,6-dicyano-1,4-hydroquinone formation, DDQH₂). An appropriate potential with respect to the reference electrode was applied and the reaction run either at controlled potential or amperostatically.

The resulting current (typically between 10–20 mA) is accompanied with development of a dark green colour at the anode. Small samples of the reaction mixture were usually analysed using HPLC-UV at intervals of known charge. After passage of the required charge, the reaction mixture was allowed to cool to room temperature and the solvents removed at a rotary evaporator. The remaining residue was dissolved in chloroform or dichloromethane (20–40 ml), filtered and poured into dilute aqueous hydrochloric acid (typically 150 ml). The organic phase was separated and the aqueous phase extracted with chloroform (typically 3 × 40 ml). The combined organic layer was washed with dilute sodium bicarbonate (typically 3 × 80 ml), water (typically 2 × 150 ml) and dried (MgSO₄). The filtered solution was evaporated under reduced pressure. The crude product mixture was purified by flash chromatography (silica grade 40–60) using chloroform as eluent. Combining and evaporation of the appropriate fractions gave the product or products in given yields. The recrystallization solvent and other details of the conditions used are given below for individual experiments.

2.2. General procedure B (large scale)

An undivided cell, constructed from a Quickfit flanged round-bottomed reaction flask, was equipped with magnetic stirrer two graphite electrodes and an Ag/AgBr reference electrode positioned close to the working electrode. It was charged with a solution containing acetic acid (460 ml), water (40 ml) and tetraethylammo-

nium tosylate (120 g; 0.4 mol; 0.8 M). The mixture was heated to 80–90 °C and the substrate added. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added in portions. The reaction mixture rapidly turns dark green (charge transfer complexation) and after about 30 min a red–pink colour develops. An appropriate potential with respect to the reference electrode was applied at the working electrode and the reaction run at either controlled potential or amperostatically. The resulting current is accompanied by a colour change, to dark green at the anode. Small samples of the reaction mixture were usually analysed using HPLC–UV at intervals of known charge consumption. The reaction was terminated after a suitable charge had been passed through the solution. The reaction mixture was allowed to cool to room temperature and the solvents evaporated off at a rotary evaporator. The remaining residue was dissolved in chloroform or dichloromethane (around 120 ml), filtered and poured into dilute aqueous hydrochloric acid (typically 350 ml). The organic phase was separated and the aqueous phase extracted with chloroform (typically 4 × 40 ml). The combined organic layer was washed with dilute sodium bicarbonate (typically 3 × 100 ml), water (typically 2 × 100 ml) and dried (MgSO₄). The filtered solution was evaporated under reduced pressure. The crude product mixture was purified by flash chromatography (silica grade 40–60) using chloroform as eluent. Combining and evaporation of the appropriate fractions gave the product or products in given yields. The recrystallisation solvent and other details of the conditions used are given below for individual experiments.

2.3. Individual electrolyses

Selected mediated electrolysis experiments are described that illustrate the various conditions used and which are cross-referenced to the entries in Tables 3 and 4.

2.3.1. DDQ mediated electrochemical preparation of 2-methoxy-6-naphthalene carboxaldehyde (**2a**). (Small scale, substrate 0.1 M, constant potential, entry 5, Table 3)

Treatment of 2-methoxy-6-methylnaphthalene (**1a**) (0.43 g; 2.5 mmol; 0.1 M) according to general procedure A, at 80 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (171 mg; 0.75 mmol; 30% equiv.) and a constant potential setting of 0.70 V (vs Ag/AgBr) resulted in a current of about 30 mA cm⁻². Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after a charge of 8.7 F, with the current reduced to about 3 mA cm⁻². Work up and purification was by flash chromatography (silica grade 40–60) using chloroform as eluent. Combining and evaporation of the appropriate fractions (*R_f*=0.6) and recrystallisation from ethanol gave the title compound (0.32 g; 1.75 mmol; 70%) as off-white microcrystals. The fraction (*R_f* < 0.3) was identified as a mixture of adducts (**5a** and **5b**).

2.3.2. DDQ mediated electrochemical preparation of 2-methoxy-6-naphthalene carboxaldehyde (**2a**). (Small scale, substrate 0.4 M, constant potential, entry 6, Table 3)

Treatment of 2-methoxy-6-methylnaphthalene (**1a**) (1.72 g; 10.0 mmol; 0.4 M) according to procedure A, at 80 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.68 g; 3.0 mmol; 30% equiv.) and a constant potential setting of 0.70 V (vs Ag/AgBr) resulted in a current of about 17.5 mA cm⁻². Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after a charge of 4.0 F, with the current reduced to about 4 mA cm⁻². Work-up and purification as described above gave after recrystallization from ethanol **2a**, (1.34 g; 7.2 mmol; 72%) as off-white microcrystals. The fraction (*R_f* < 0.3) was identified as a mixture of adducts (**5a** and **5b**).

2.3.3. 2-Methoxy-6-naphthalene carboxaldehyde (**2a**). (Large scale, substrate 0.4 M, constant potential, entry 8, Table 3)

Treatment of 2-methoxy-6-methylnaphthalene (**8a**) (34.4 g; 0.2 mol; 0.4 M) was oxidized according to procedure B, at 85 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (11.4 g; 0.05 mol; 25% equiv.) and a constant potential setting of 0.55 V (vs Ag/AgBr) at an initial current of about 16 mA cm⁻². A graphite anode was used. Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after a charge of 5.3 F, with the current at about 3 mA cm⁻². Work up and purification as before gave the title compound (26.44 g; 0.142 mol; 71%) as off-white microcrystals. The fraction (*R_f*=0.5) gave traces of 2-(α -acetoxymethyl)-6-methoxy-naphthalene (**5b**).

2.3.4. DDQ mediated oxidation of 2-(α -hydroxymethyl)-6-methoxynaphthalene (**1k**)

Treatment of 2-(α -hydroxymethyl)-6-methoxy-naphthalene (**1k**) (1.88 g; 0.01 mol; 0.4 M) was electrolysed according to procedure A, at 85 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.57 g; 2.5 mmol; 25% equiv.) and a constant potential of 0.55 V (vs Ag/AgBr) at an initial current of about 22 mA cm⁻². Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after a charge of 2.3 F, with the current reduced to about 5 mA cm⁻². Work-up and purification by flash chromatography (silica grade 40–60) using chloroform as eluent followed. Combining and evaporation of the appropriate fractions (*R_f*=0.6) and recrystallization from ethanol gave 2-methoxy-6-naphthalene carboxaldehyde (**1a**) (1.40 g; 7.5 mmol; 75%) as off-white micro crystals.

2.3.5. DDQ mediated oxidation of 2-(α -acetoxymethyl)-6-methoxynaphthalene (**II**)

Electrolysis of 2-(α -acetoxymethyl)-6-methoxynaphthalene (**II**) (2.30 g; 0.01 mol; 0.4 M) according to procedure A, at 85 °C, using 2,3-dichloro-5,6-dicyano-1,

4-benzoquinone (0.57 g; 2.5 mmol; 25% equiv.) and a constant potential of 0.55 V (vs Ag/AgBr) gave an initial current of about 24 mA cm⁻². Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after passage of 2.4 F, with the current reduced to about 5 mA cm⁻². Work-up and purification as above gave 2-methoxy-6-naphthalene carboxaldehyde (**1a**) (1.55 g; 8.3 mmol; 83%) as off-white microcrystals.

2.3.6. 2-Methoxy-6-naphthalene carboxaldehyde (2a). (Small scale, substrate 0.4 M, constant current, entry 7, Table 3)

2-Methoxy-6-methylnaphthalene (**1a**) (1.72 g; 0.01 mol; 0.4 M) was electrolysed at a constant current of 10 mA according to procedure A, at 85 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.57 g; 2.5 mmol; 25% equiv.). A graphite anode (about 1.6 cm², 6.7 mA cm⁻²) was used. Tetraethylammonium tosylate (0.8 M) was the supporting electrolyte. The reaction was terminated after a charge of 4.0 F. Work-up and purification was by flash chromatography (silica grade 40–60) using chloroform as eluent. The title compound (1.32 g; 7.1 mmol; 71%) was obtained as off-white microcrystals.

2.3.7. 2-Methoxy-6-naphthalene carboxaldehyde (2a). (Large scale, substrate 0.2 M, constant potential, entry 8, Table 3)

2-Methoxy-6-methylnaphthalene (**1a**) (34.4 g; 0.2 mol; 0.4 M) was electrolysed at a constant current of 250 mA according to procedure A, at 90 °C, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (11.4 g; 0.05 mol; 25% equiv.). A graphite anode (about 35 cm², 7.1 mA cm⁻²) was used. Tetraethylammonium tosylate (0.73 M) was the supporting electrolyte. The reaction was terminated after a charge of 5.8 F. Work-up and purification was as before and gave **2a** (26.44 g; 0.142 mol; 71%) as off-white microcrystals.

2.3.8. DDQ mediated preparation of 2-naphthyl 4-methoxyphenyl ketone (2e). (Entry 3, Table 4)

2-(4-Methoxybenzyl)-naphthalene (**1e**) (0.40 g; 1.61 mmol) was oxidized at controlled potential according to procedure A, using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.091 g; 0.40 mmol). After passage of 4.7 F the initial current of 15 mA had fallen to 3 mA. Work up and purification was by flash chromatography (silica grade 40–60) using chloroform as eluent. Recrystallization of the crude product from ethanol gave **2e** (320 mg; 76%) as pale pink crystals.

Starting material (70 mg; 17%) was recovered and HPLC-UV and NMR confirmed the formation of a trace of 2-(α -acetoxy-4-methoxybenzyl)-naphthalene (**4e**).

3. Results and discussion

The substrates used in this study are displayed as formulae **1a–1l** and the likely products as **2–5**. The

adducts **5a–b** are included as **5a** was found [7] to be a byproduct in batch DDQ oxidation of 2-methyl-6-methoxynaphthalene (**1a**) in dry benzene; the adduct (**5b**) turns out to be additionally formed in DDQ oxidations in acetic acid (see later).

3.1. Cyclic voltammetry and DDQ regeneration

That DDQ can be regenerated by anodic oxidation is shown by cyclic voltammetry (Figure 1), which displays chemical reversibility at modest scan rates, with large peak separations that suggest that both the oxidation and reduction processes are electrochemically irreversible. Furthermore the anodic peak potentials are affected by solvent changes much more than are the reduction peak potentials (Table 1). A plausible mechanism that is consistent with the observation of chemical reversibility is given in Scheme 1.

Table 2 includes data relating to electron-rich 2-alkyl and 2-benzyl naphthalenes that, on the basis [7] of batch DDQ oxidations, offer good prospects for mediated reaction. Cyclic voltammetry of a mixture of DDQH₂ and 2-methyl-6-methoxynaphthalene (**1a**), in dry acetic acid, shows (Figure 2) that in practice DDQH₂ can be oxidized at a less anodic potential than (**1a**). At room temperature the DDQ thus generated reacts very slowly with the naphthalene derivative and its presence is evident from the reduction peak at about 0.2 V vs Ag/AgBr. This is consistent with the results of batch DDQ oxidations [7] in acetic acid for which reaction at 80 °C was required. However, the results indicate that in

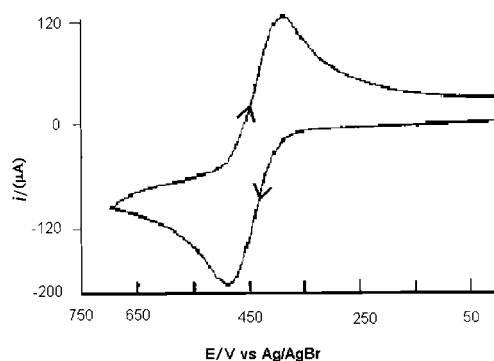


Fig. 1. Cyclic voltammetry of DDQH₂ (0.3 V s⁻¹, HOAc/H₂O 85:15 vol %; Et₄NOTs 0.5 M).

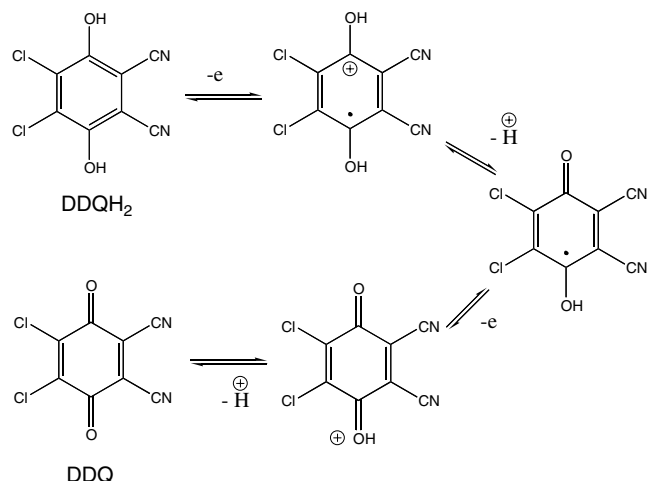
Table 1. Cyclic voltammetry* for DDQH₂/DDQ

| Substrate | Supporting electrolyte | Solvent | E_{pa} | E_{pc} | ΔE_p |
|-------------------|----------------------------------|------------------------------------|----------|-------------------|--------------|
| DDQH ₂ | Et ₄ NOTs | HOAc/H ₂ O [†] | 0.49 | 0.39 | 0.10 |
| DDQH ₂ | Et ₄ NOTs | HOAc | 0.85 | 0.28 | 0.57 |
| DDQH ₂ | Et ₄ NBF ₄ | MeCN | 1.51 | 0.50 | 1.01 |
| DDQ | Et ₄ NBF ₄ | MeCN | – | 0.51 [‡] | – |

* Pt anode, 0.3 V s⁻¹, Et₄NOTs 0.5 M, Et₄NBF₄ 0.1 M; V vs Ag/AgBr.

[†] 85/15 (v/v).

[‡] vs. Ag/AgCl, [8].



Scheme 1.

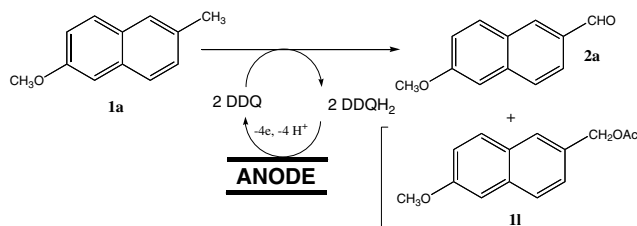
Table 2. Oxidation potentials* for 2- and 6- substituted naphthalenes

| Compound | 6-Substituent | 2-Substituent | E_p^1/SCE |
|-----------|-------------------|-------------------------------------------------------------------|--------------------|
| 1a | OCH ₃ | CH ₃ | 1.41 |
| 1b | H | 4-CH ₃ O.C ₆ H ₄ CH ₂ | 1.79 |
| 1c | H | 4-Cl.C ₆ H ₄ CH ₂ | 1.82 |
| 1d | CH ₃ O | C ₆ H ₅ | 1.41 |
| 1e | CH ₃ O | 4-CH ₃ .C ₆ H ₄ CH ₂ | 1.42 |
| 1f | CH ₃ O | 4-CH ₃ O.C ₆ H ₄ CH ₂ | 1.41 |
| 1g | CH ₃ O | 4-Cl.C ₆ H ₄ CH ₂ | 1.50 |

* Irreversible oxidation in all cases at substrate concentration 2–3 mM, $n = 0.6 \text{ V s}^{-1}$, CH₃CN–Bu₄NBF₄ (0.1 M), Pt anode (0.5 mm dia.), Ag/AgNO₃ (0.1 M).

[†] Calibrated against the reversible redox couple for 9,10-diphenylanthracene ($E^\circ = 0.85 \text{ V vs Ag/Ag}^+$, 1.22 V vs SCE) [9, 10].

principle DDQ oxidations of electron-rich 2-alkyl and 2-benzyl naphthalenes can be carried out with *in situ* anodic regeneration of DDQ from DDQH₂. The overall process is illustrated for **1a** in Scheme 2 and the practical difficulties to be overcome include operation at a temperature at which the rate of reaction between substrate and DDQ is matched to the oxidation of DDQH₂. As outlined in Scheme 1, the conversion of



Scheme 2.

DDQH₂ into DDQ is not straightforward and is a multistep process.

3.2. Optimization experiments

The optimum conditions for batch oxidation of 2-methoxy-6-methylnaphthalene (**1a**) with DDQ involved aqueous acetic acid (~10% v/v), 80 °C, and a threefold molar excess of DDQ. There would be little advantage in the anodic method if the excess of DDQ were to be so high so a decision was taken to explore much lower ratios of DDQ:**1a**. Furthermore, a successful process would need to convert a relatively high concentration of **1a** and ultimately to run at constant current, in an undivided cell with a cheap anode material.

A selection of the many optimisation experiments performed is included in Table 3. The supporting electrolyte was chosen to be tetraethylammonium tosylate, which is cheap and highly soluble in aqueous acetic acid. Subsequent experiments with a range of other cheap electrolytes such as potassium fluoride and potassium acetate showed them to be less satisfactory. Initial small-scale experiments (entries 1–3, substrate about 2 g, cell volume 25 ml) were run in a divided cell at constant potential with a platinum anode hopefully to exclude complications from competing oxidation of DDQH₂ and **1a** and reduction of products at the cathode. The experiments in entries 1–3 are characterized by the formation of substantial amounts of the dimer **3**. From our earlier work we know this to be a major product of direct anodic oxidation of **1a**, arising by coupling of the intermediate radical cation. Changing

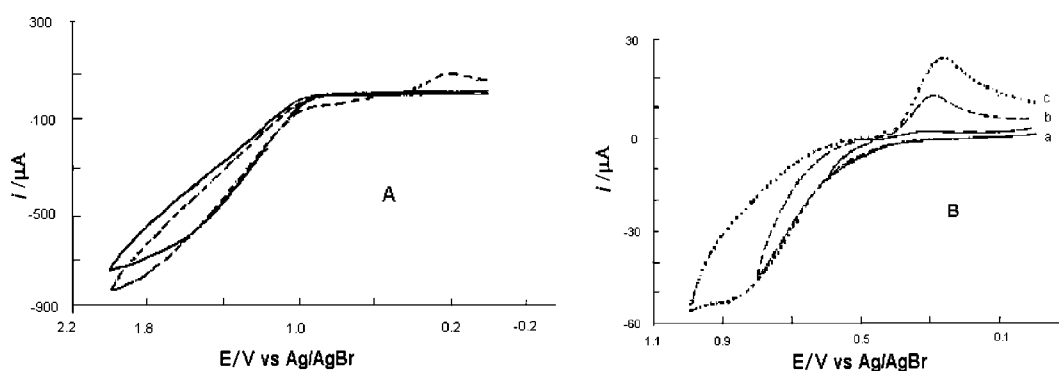


Fig. 2. (A) Cyclic voltammetry of 2-methoxy-6-methylnaphthalene (**1a**) (alone, solid line) and in the presence of DDQH₂ (dotted line); (B) Mixture of (**1a**) and DDQH₂, (a) reversal at about 0.6 V, (b) reversal at 0.8 V, (c) reversal at 1.0 V (Pt anode, HOAc–Et₄NOTs 0.5 M, 0.3 V s⁻¹).

Table 3. DDQ mediated electrolyses of 2-methoxy-6-methylnaphthalene (**1a**) in HOAc–H₂O (8 vol %)

| Reaction conditions | | | | | | | | | Products/% | | | |
|---------------------|---------------------|------------|-----------------------------|-----------|----------|-------|-------------|---------------|----------------|--------------------|-----------|-----------------------|
| Entry | Concn. 1a /M | Concn. DDQ | Concn. Et ₄ NOTs | Charge /F | Temp /°C | Anode | Cell type | Conversion /% | Dimer 3 | Aldehyde 2a | 11 | Adducts 5a, 5b |
| 1 | 0.06 | 0.03 | 0.1 | 1.7 | 70 | Pt* | Divided | 65 | 30 | 13 | 14 | – |
| 2 | 0.1 | 0.01 | 0.1 | 3.5 | 90 | Pt* | Divided | 74 | 44 | 30 | – | – |
| 3 | 0.1 | 0.02 | 0.5 | 2.2 | 80 | Pt† | Divided | 65 | 14 | 37 | – | – |
| 4 | 0.2 | 0.06 | 0.8 | 4.0 | 80 | C† | Undivided | 56 | – | 47 | – | 4 |
| 5 | 0.1 | 0.03 | 0.8 | 8.7 | 80 | C† | Undivided | 92 | – | 70 | – | 13 |
| 6 | 0.4 | 0.12 | 0.8 | 4.0 | 80 | C† | Undivided | 90 | – | 72 | – | 16 |
| 7 | 0.4 | 0.1 | 0.8 | 4.0 | 85 | C‡ | Undivided§ | 89 | – | 71 | – | 18 |
| 8 | 0.4 | 0.1 | 0.7 | 5.8 | 90 | C‡ | Undivided** | 87 | – | 71 | – | 16 |

* at 0.85 V vs. Ag/AgBr.

† at 0.7 V.

‡ at 7 mA cm^{–2}.

§ S/V ratio 0.1, cell volume 25 ml.

** S/V ratio 0.07, cell volume 500 ml.

the anode potential from 0.85 to 0.70 V (entry 3) was sufficient to improve the selectivity and reduce competing direct oxidation of **1a**. Although at this stage the yield of aldehyde **2a** was low (37%) it was achieved with only 10 mol % of DDQ. A disadvantage of platinum, in addition to the overriding one of cost, was that it became fouled and passage of the required charge was difficult.

Graphite anodes proved to be much more suitable. In an undivided cell, but at controlled potential (entries 4 and 5), the yield of **2a** and the conversion of **1a** were found to be improved by operation at reduced substrate concentration and the passage of an excess of charge. This was at the expense of increased formation of adducts (**5a** and **5b**). Fine tuning of the conditions for electrolysis at a graphite anode and in an undivided cell led to highly satisfactory results (entries 7 and 8). These employed reasonable concentrations of **1a**, a relatively low proportion of DDQ and a constant current that was low enough to give selective oxidation of DDQH₂ but which led to long reaction times (2–3 days) with the given ratios of anode surface area to volume (S/V). The last entry describes the conditions whereby electrolyses at a 35 g scale could be conducted; the simply con-

structed 500 ml volume cell used is described in the experimental section. Further improvement depends on the application of cells with high S/V ratios, for which there is good precedent [11].

3.3. DDQ mediated side-chain oxidation of 2-benzyl-naphthalene derivatives

As part of the earlier, mechanistically oriented study [7] the direct anodic side-chain oxidation in methanol of 2-benzyl-naphthalene derivatives such as **1c–1j** was attempted. Initially it was expected that deprotonation of the first-formed radical cation would be enhanced because the ensuing radical would be benzylic. In the event deprotonation with subsequent side-chain oxidation was observed in low yield and only for the electron rich example, **1e**. The substrates **1c**, **1d** and **1f** underwent nuclear substitution to a mixture of 9,10-methoxylated derivatives and the corresponding 9,10-naphthoquinone.

The optimum electrolysis conditions determined for the DDQ mediated conversion of 2-methoxy-6-methylnaphthalene (**1a**) were used to oxidize several differently substituted 2-benzyl-naphthalenes (Table 4). Only the more electron-rich substrates were converted into the

Table 4. DDQ mediated electrolyses* of 2- and 6-substituted naphthalenes in aqueous acetic acid (8% v/v)

| Entry | 2-Substituent | 6-Substituent | Charge /F | Conversion† /% | ArCOAr'⁺ /% | ArCH(OAc)Ar'‡ (4) /% |
|-------|----------------------------------------------------------------------------------|-------------------|-----------|----------------|-------------|----------------------|
| 1 | C ₆ H ₅ .CH ₂ (1c) | H | 5.6 | <10 | 0 | 0 |
| 2 | 4-CH ₃ .C ₆ H ₄ .CH ₂ (1d) | H | 6.2 | <10 | 0 | 0 |
| 3 | 4-CH ₃ O.C ₆ H ₄ .CH ₂ (1e) | H | 4.7 | 83 | 76 | <5 |
| 4 | 4-Cl.C ₆ H ₄ .CH ₂ (1f) | H | 4.5 | 82 | 71 | 5 |
| 5§ | C ₆ H ₅ .CH ₂ (1g) | CH ₃ O | 5.3 | 93 | 72 | 13 |
| 6§ | 4-CH ₃ .C ₆ H ₄ .CH ₂ (1h) | CH ₃ O | 4.7 | 88 | 64 | 16 |
| 7 | 4-CH ₃ O.C ₆ H ₄ .CH ₂ (1i) | CH ₃ O | 4.5 | 90 | 73 | 7 |
| 8 | 4-Cl.C ₆ H ₄ .CH ₂ (1j) | CH ₃ O | 4.8 | 92 | 71 | 9 |

* Graphite anode, Et₄NOTs (0.8 M), constant potential (0.55 V vs Ag/AgBr, 85 °C, substrate 0.05 M, DDQ 12.5 mM).

† Calculated from reclaimed starting material.

‡ Isolated yields, Ar = naphthyl, Ar' = 4-R-benzyl.

§ Substrate 0.1 M, DDQ 25 mM.

corresponding ketones, but where the method works it works well. As for the 2-methoxy-6-methylnaphthalene (**1a**) case adduct formation becomes more prominent at the higher substrate concentrations.

3.4. Reaction profile

As discussed in the earlier paper [7], the mechanism of DDQ oxidation involves prior formation of charge transfer complexes between the electron-rich substrates and the electron-poor DDQ, followed probably by hydride transfer. The possibilities using 2-methoxy-6-methylnaphthalene (**1a**) as an example are summarised in Scheme 3, which also accounts for adduct formation. The proposed route also requires the intermediacy of compounds of the type **1k** and **1l**, which are known to be efficiently oxidized with DDQ under batch conditions [7] and which were also shown here to be oxidized to the corresponding carbonyl compounds by DDQ-mediated electrolysis (Section 2).

Using the conditions given in Table 3, entry 8, the course of electrolysis was followed by HPLC analysis of reaction mixture components as a function of time. The results are given in Figure 3. The products are present at zero charge because the experiment involves initial treatment with 20 mol % of DDQ with subsequent

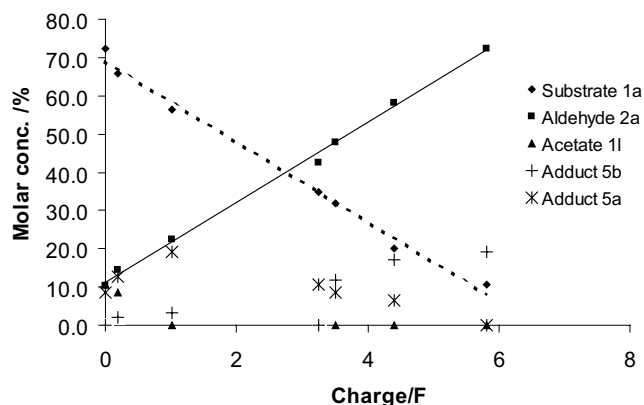
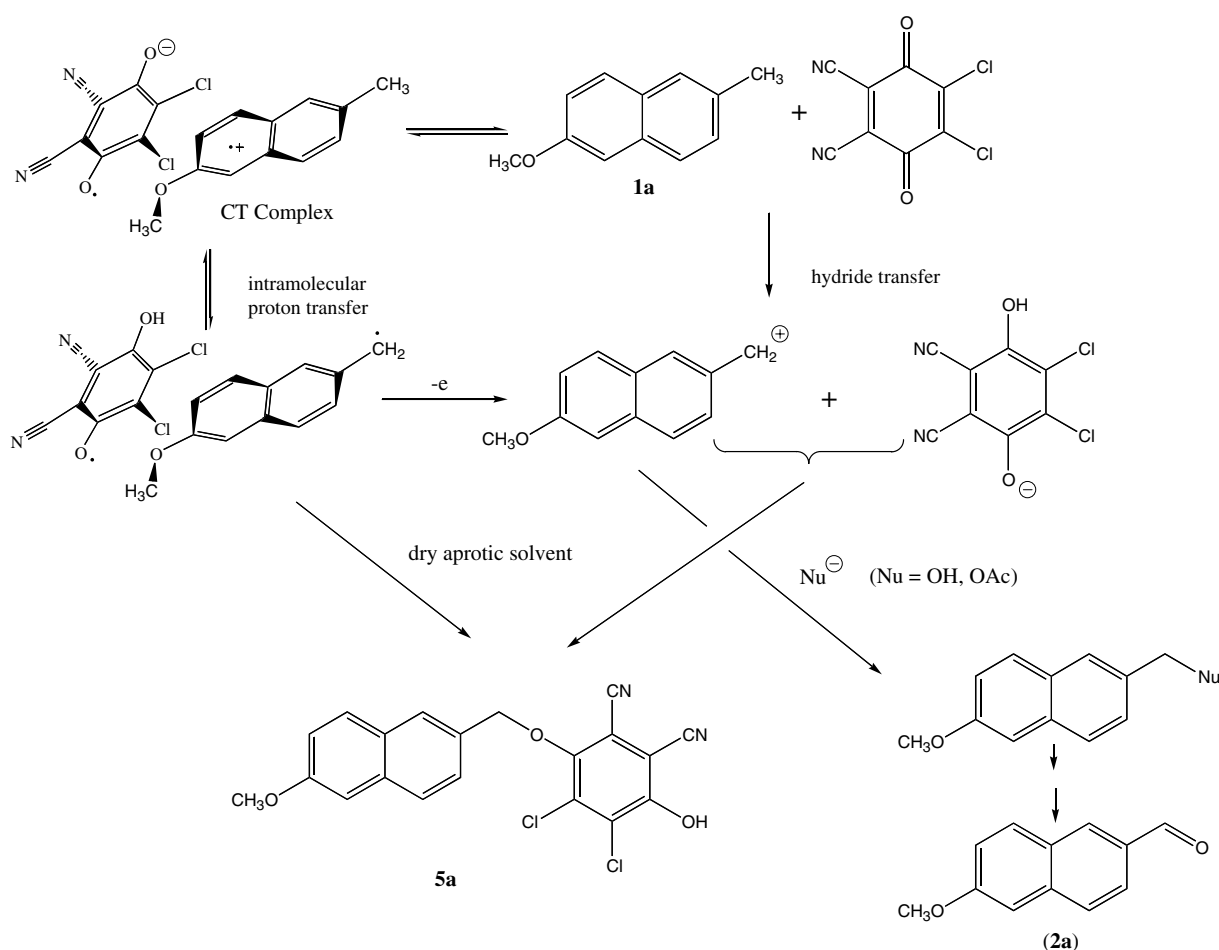


Fig. 3. Reaction profile for DDQ mediated electrolysis of 2-methoxy-6-methylnaphthalene (**1a**).

reoxidation of the DDQH₂ that is formed. The steady formation of the aldehyde **2a** is evident, concomitant with the decay of the starting material **1a**. Initially the adduct **5a** is present, but as reaction proceeds this is converted by further oxidation into **5b**; these reactions appear to parallel aldehyde formation and the adducts are byproducts that do not lie on the pathway to aldehyde. Although initially present, the acetate **1l** is rapidly oxidised, presumably into the aldehyde **2a**, in



Scheme 3.

line with the results of batch oxidations with DDQ and also the DDQ mediated electrolyses of **1k** and **1l** described in the experimental section.

The formation of the aldehyde **2a** and conversion of the substrate **1a** consume more than the theoretically required 4 F. This is probably due to concurrent (Kolbe) oxidation of the solvent (CH₃CO₂H), known to occur at relatively low potentials at graphite anodes [12].

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